A STUDY OF ENERGY TRANSFER PROCESSES IN MOLECULAR LASERS

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Quarterly Technical Report

The research carried out under this contract is divided into four tasks, indicated as follows in the work statement.

(1) Application of currently available close coupling codes to the calculation of cross sections of interest to the molecular lasers under consideration (initially N_2, N_2O, CO_2 and CO),

(2) Extension of the existing computer program for the vibrational population distribution of a binary mixture of gases to include excitation and de-excitation processes specific to the laser mixtures of interest, making use of the results of the close-coupling calculations, as they become available.

(3) Application of the spectroscopic observation of side light and small signal gain measurements to the determination of vibrational and rotational population distributions in the molecular laser systems under study (initially CO_2 and CO).

(4) Preliminary computer modeling of the laser system, to include the effects of spatial variation of electron density and temperature and gas temperature.

Progress to date has been as follows:

1. Cross Section Calculations

Cross sections for the vibrational excitation of CO from the ground to the first excited level by collision with He, Ne and Ar have been calculated at various collision energies as shown in

Table 1, using a Lennard-Jones (6-12) potential to represent the interaction, and retaining coupling between the first 3 or 4 vibrational states of CO.

TABLE 1.

Collision energy (eV)	0.6	0.8	1.0	1.5	2.0
Helium $Q_{01}(\pi a_o^2)$	* $.16^{-1}$	$.84^{-1}$	.241	-	-
Neon $Q_{01}(\pi a_o^2)$	$.235^{-4}$	$.55^{-3}$	$.39^{-2}$	$.66^{-1}$	.295
Argon $Q_{01}(\pi a_o^2)$	-	$.983^{-5}$	$.159^{-3}$	$.565^{-2}$	-

*superscript denotes the power of 10 by which the number must be multiplied.

On the basis of these cross sections the vibrational relaxation times for CO in the corresponding gases can be calculated and compared with the experimental measurements of Millikan et al.[1]

The theoretical results for helium are low by a factor of 90, for neon the results are low by a factor of 7 and for argon the results are low by a factor of 4. These comparisons indicate that the Q_{01} for the corresponding cases are too large by the same factors.

To establish why the model, which was satisfactory for pure CO[2], is not as good for the inert gases, the CO-Ar system has been studied in detail.

Recent measurements of Jordan et al.[3] indicate that the r^{-12} core of the Lennard-Jones potential is too strong, and that it should be replaced by r^{-7}. A semi-empirical soft core potential has been constructed which fits the Jordan data for small r and still follows the Lennard-Jones potential at large r (Technical

Report #2, April 26 to July 31, 1970). This potential reduces the coupling between the vibrational states by about a factor of 2 as can be seen in Table 2 which shows as an example the matrix elements from both potentials at a collision energy of 1.5 eV and zero impact parameter.

TABLE 2. Matrix Elements at 1.5 eV Collision Energy

Potential	V_{00}	V_{01}	V_{11}	V_{20}	V_{21}	V_{22}
Lennard-Jones	1.0000	.0820	1.0067	.0048	.1164	1.0135
Soft Core	1.0000	.0493	1.0024	.0017	.0698	1.0049

Potential	V_{30}	V_{31}	V_{32}	V_{33}
Lennard-Jones	.0002	.0083	.1430	1.0203
Soft Core	.0000	.0030	.0856	1.0073

This reduction in coupling leads in turn to a reduction in the excitation cross section. However, it is found that the reduction goes considerably beyond what is required to produce agreement between the theoretical and experimental vibrational relaxation times. Cross sections obtained on the basis of coupling two vibrational states yields a relaxation time some 50 times longer than the experimental value. Coupling in additional vibrational states is found to further reduce these cross sections, unlike previous calculations where coupling in higher states in general yielded an increase.

The possibility that this behaviour is a numerical consequence of the much weakened coupling between the scattering equations has been investigated. It is found that the solutions are quite stable and it can only be concluded that the results obtained are in fact correct for the soft core potential assumed.

A final report giving the details of this work is in process of preparation.

Further calculations are currently underway on both the N_2-Ar and CO-He systems, using appropriate soft core potentials, in order to determine whether the disagreement of theory with observation is specific to the CO-Ar system or is common to all collisions when a "soft" interaction is assumed.

2. Vibrational Distributions and 4. Plasma Properties

The numerical code which models the transient behaviour of a binary mixture of diatomic molecules (N_2 and CO) in the presence of both inert diluent and hot electrons is nearly operational. The rate coefficients for the excitation of the v=o vibrational level of N_2 and CO have been calculated as a function of electron temperature from the data of Schulz[4]. Scaling of these rate coefficients to describe the excitation of the higher lying vibrational levels is being accomplished using the pseudo potential calculations of Chen[5]. It is expected that this entire program will be operational in the next 2 weeks and model calculations on the transient behavior of the vibrational populations appropriate to a N_2-CO-He pulsed direct discharge molecular laser will commence. In addition, the time integration will be extended such that quasi-steady state distributions can be modeled as appropriate to CW laser operation.

The binary mixture vibrational relaxation code without the electron terms has been used for further predictions on the reaction of H_2 and O_2, vibrationally excited by stimulated Raman scattering. By using this code, together with model reaction rate coefficients between vibrationally excited H_2 and D_2 to form HD,

we have concluded that the most informative experiment to perform on this reaction mixture is to preferentially excite the D_2 (v=1) mode rather than the H_2 (v=1) mode as is currently being done. This conclusion stems from the fact that initial excitation of H_2 (v=1) is followed by rapid redistribution of the H_2 vibrational energy with subsequent exothermic transfer via vibration exhange processes to D_2 vibrational energy (due to the smaller vibrational spacing of the D_2 compared to H_2). The transient behavior of selected levels of the Raman excited H_2-D_2 system diluted by Argon is shown in figure 1. The model predictions of HD formation due to both vibrationally excited D_2 and H_2 is shown in figure 2 for the same conditions. A second run in which the D_2 was initially excited almost entirely via the excited D_2 reaction, i.e.,

$$D_2 \text{ (vib)} + H_2 \rightarrow 2HD$$

rather than

$$H_2 \text{ (vib)} + D_2 \rightarrow 2HD$$

This information has been transmitted to Professor Simon Bauer at Cornell University for consideration in his experimental program. No further model calculations are planned on this reaction system until new experimental data becomes available.

3. Optical Diagnostic Experiments

In order to test the laser computer model, a program of optical diagnostic measurements has been initiated. Eventually, measurements from roughly 2,000 A to 15μ will be made on the CO_2 and CO laser systems. The majority of the equipment necessary for these measurements has been assembled, partially with Wayne State University funds. This equipment includes a Jarrel Ash ¼m

double monochrometer, SBRC Cu doped Ge detector, Au/Ge, PbS and PbSe detectors.

Because of the evident importance of a diagnostic for the spontaneous emission from CO_2, the first trials performed during this reporting period employed the PbSe detector and the Au/Ge detectors to monitor simultaneously the spontaneous emission from the v_3 fundamental and the induced emission respectively. For these preliminary measurements no modifications to the existing laser system were made. Measurements were made from the end port using a B & L grating blazed at 5μ as illustrated in figure 3. This configuration is being modified to permit side viewing perpendicular to the laser axis, but several important observations have been made using this crude preliminary configuration.

(1) Efficiency of CO in $CO_2(v_3)$ excitation

One important parameter which could be well identified from the present work is the relative efficiency of CO as the main energy transfer source compared to N_2. In figure 2, the spontaneous and induced emissions from the CO_2 laser were monitored as a function of the fraction of CO in the system at constant total pressure. When the N_2 has been totally replaced by CO, both the spontaneous and the induced emission have been reduced by about 30-35%. The scatter in the induced emission data was due largely to long term instabilities associated with made shifts then present in the laser system. As also illustrated in Figure 2, the systematic trend in the emission decline may not be attributed to a decline in the electron energy. The laser power supply is current regulated; the variation of the applied voltage, while systematic and small, is tending to increase the input power for 100% CO over a 100% N_2 system. The spacings between the 0-1 levels of $CO_2^{(v_3)}$, N_2 and CO are 2349, 2331 and

2134 cm^{-1} respectively. This leaves an 18 cm^{-1} energy defect for $N_2^{\mp}$-CO_2 collisions and a 206 cm^{-1} energy defect for $CO^{\mp}$-CO_2 collisions. For the Rapp-Englander Golden model, which is not applicable in any rigorous fashion but may give some insight, this energy defect would make the rate constant[6] for $CO^{\mp}$- CO_2. Vibrational energy exchange (VV) an order of magnitude slower than $N_2^{\mp}$-CO_2 VV at 300°K. In addition, of course, there will be some losses of energy from the $CO^{\mp}$ due to spontaneous emission at 4.65μ. Thus, Figure 4 suggests that VV may not be the rate controlling step in the CO_2 laser unless the $CO^{\mp}$- CO_2 VV rate constant is larger than anticipated.

(2) Two Color Measurements As a Function of CO_2 Partial Pressure

In this series of experiments, the total pressure, P_{tot}, maintained constant at 9.480 Torr by replacing CO_2 with Ar. A typical plot of the resulting data is given in Figure 5. Spontaneous Emission is observed over the entire range of CO_2 concentrations observed. A definite threshold for stimulated emission was found to exist. While not accurately defined in Figure 5 because of experimental error, there is little doubt that a threshold exists because there is no signal to noise problem on the Au/Ge detector channel. As suggested by Figure 5, the threshold occurs near the maximum in the spontaneous emission. It is not clear from end on measurements whether the maximum in the spontaneous emission corresponds to an excited $CO_2^{\mp}(v_3)$ maximum or whether increased $CO_2^{\mp}(v_3)$ is balanced by self absorption. Thus, the most important feature of figure 5 is the threshold behavior and not the high CO_2 concentration behavior. The threshold will be better defined for future computer modeling. A potential complicating factor in the interpretation of this data will be the effect of Ar, which was to decrease the intensity of the stimulated emission--without significant effect upon the spontaneous emission!

(3) Two Color Measurements As a Function of N_2 Partial Pressure

No threshold behavior above 0 was observed when N_2 was replaced by Ar, as illustrated in Figure 6. Of considerable interest is the fact that the spontaneous emission did not disappear, suggestive of alternative $CO_2^{\mp}(v_3)$ excitation mechanisms besides N_2 VV. The stimulated emission was linear in the N_2 concentration up to 0.2 Torr.

(4) CO_2 - He Stimulated Emission

Stimulated emission has been observed in the absence of added N_2 of CO, suggesting that significant quantities of CO_2 are dissociated directly or indirectly by e collisions:

$$CO_2 + e \rightarrow CO + O + e$$

or,

$$CO_2 + e \rightarrow CO_2 + 2e$$

followed by,

$$CO_2^+ + e \rightarrow CO + O$$

Under optimum conditions (4.5 Torr total) the CO_2-He laser is only about 10% as efficient as the N_2-CO_2-He laser. Again, explanation awaits the computer model, since an alternative explanation would involve direct excitation of $CO_2^{\mp}(v_3)$ via electron collision.

In summary, the preliminary experiments have suggested the need for additional mechanisms not previously suggested in the established mechanism[7]. In Table I, we have summarized possible explanations which must be added to the computer model.

Table 2.

Reaction	Need
$e + N_2(o) \rightleftarrows N_2^{\mp}(1) + e$	To excite CO_2-N_2-He laser
$e + CO_2 \rightarrow CO + O + e$	To provide CO for CO_2-He laser
$e + CO \rightleftarrows CO^{\mp} + e$	To excite CO_2-CO-He laser
$N_2^{\mp}(i) + N_2(i) \rightleftarrows N_2^{\mp}(i+1) + N_2^{\mp}(i-1)$	Same for CO, CO_2
$N_2^{\mp}(1) + CO_2(o) \rightarrow N_2 + CO_2^{\mp}(001)$	Excitation
$CO^{\mp}(1) + CO_2 \rightarrow CO + CO_2^{\mp}$	Excitation
$CO_2^{\mp}(001) \rightarrow CO_2(o) + h\nu(4.3\mu)$	Spontaneous emission
$CO_2^{\mp}(001) + h\nu \rightarrow CO_2^{\mp}(010) + h\nu(10.6\mu) + h\nu$	Stimulated emission
$CO_2^{\mp}(010) + H_2 \rightarrow CO_2^{(100)} + H_2$	To create inversion
$CO_2^{\mp}(010) + He \rightarrow CO_2^{(100)} + He$	To create inversion
$CO_2(100) + He \rightarrow CO_2(o) + He$	To create inversion
$N_2^{\mp}(1) + O \rightarrow N_2(o) + O$	To explain decrease in stimulation with excess CO_2?
$CO^{\mp} + O \rightarrow CO + O$	To explain decrease in stimulation with excess CO_2?
$O + O + M \rightarrow O_2 + M$	To help quench discharge?
$e + O_2 + M \rightarrow O_2^{-} + M$	To help quench discharge?
$e + A \rightarrow e + A + KE$?	To explain quenching of stimulated emission by A

References

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7. Taylor and Bitterman, Rev. Mod. Phys., 41, 26 (1969).

Figure 1

H_2 AND D_2 VIBRATIONAL RELAXATION IN AN ARGON DILUENT

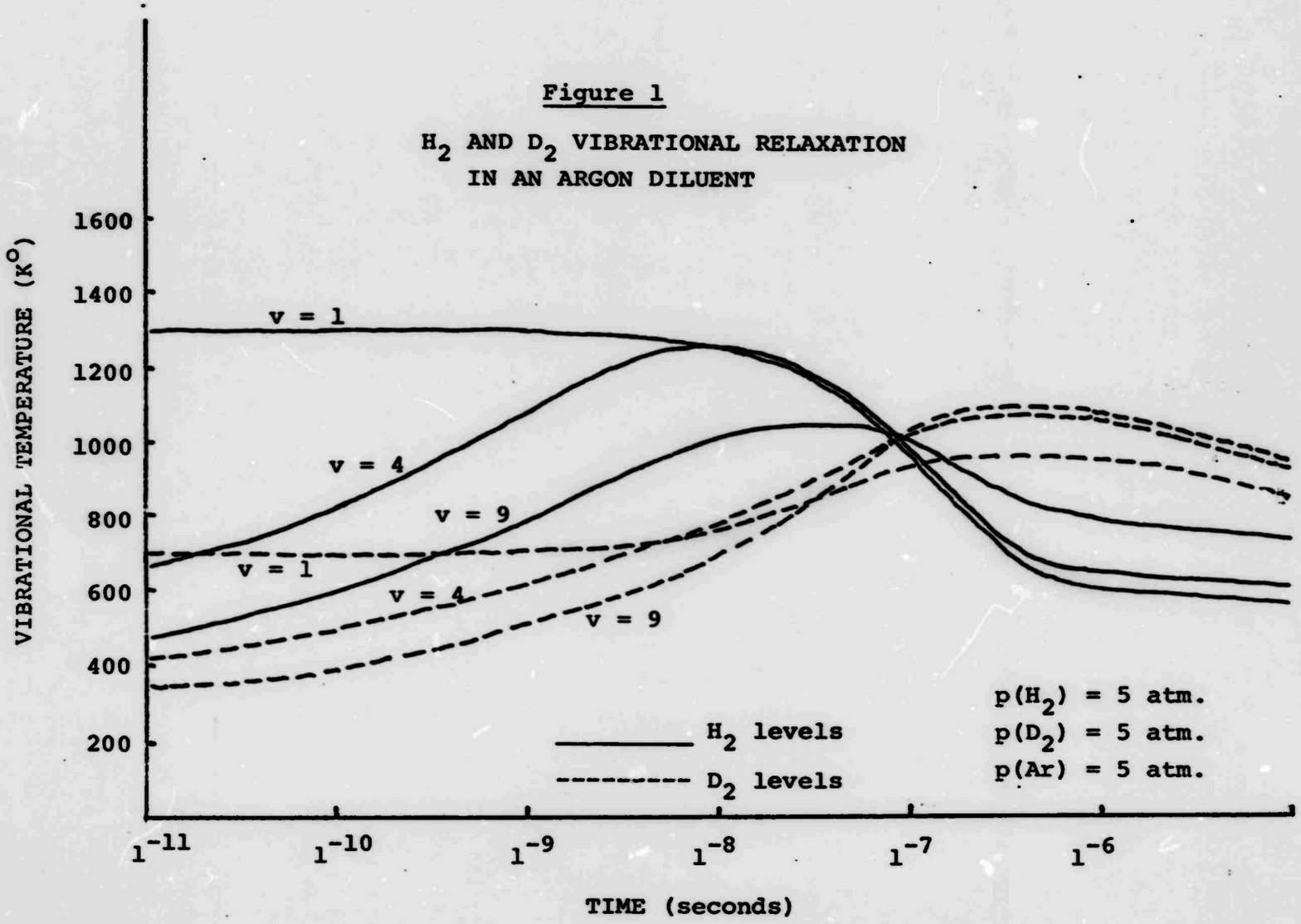
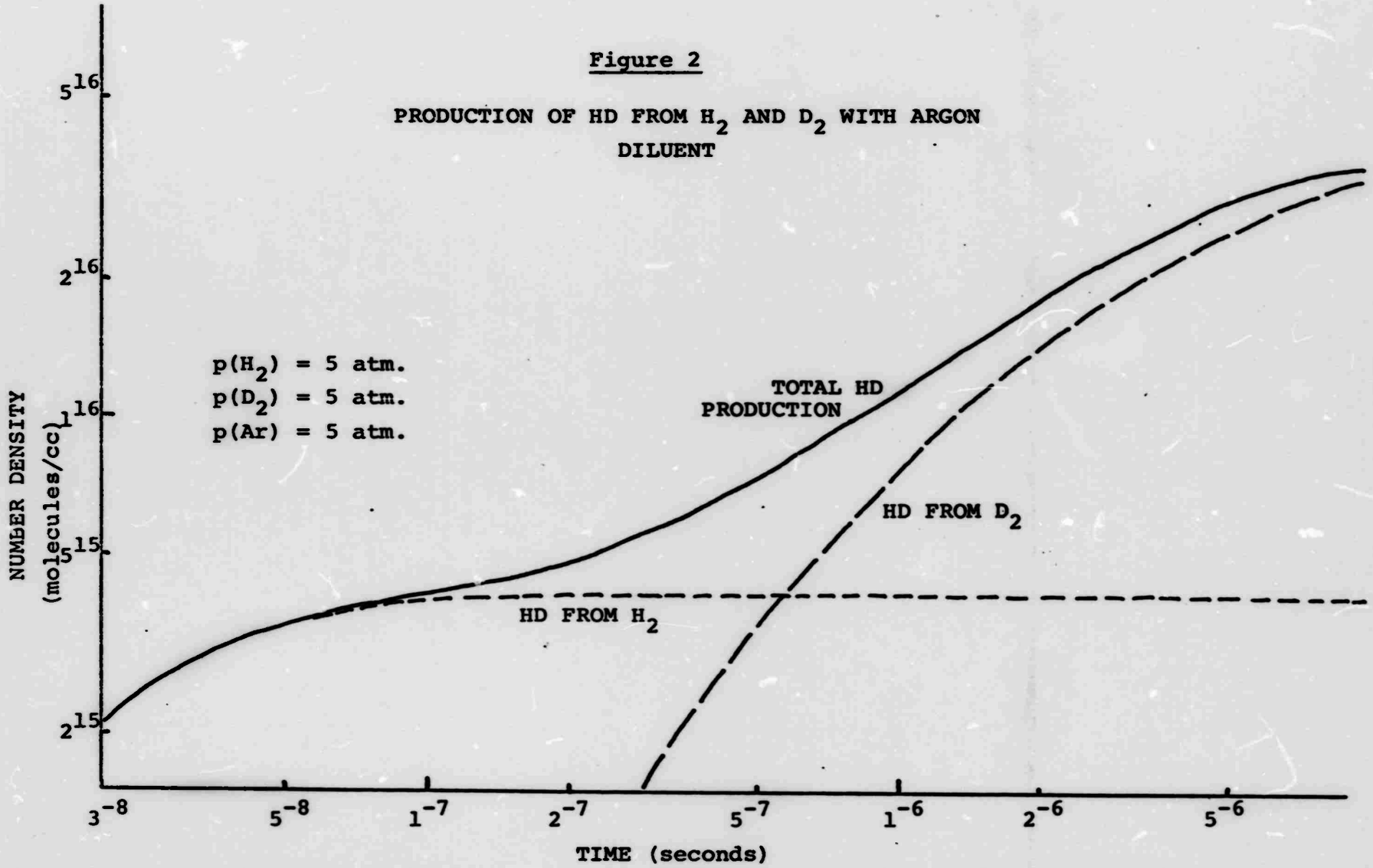


Figure 2

PRODUCTION OF HD FROM H_2 AND D_2 WITH ARGON DILUENT



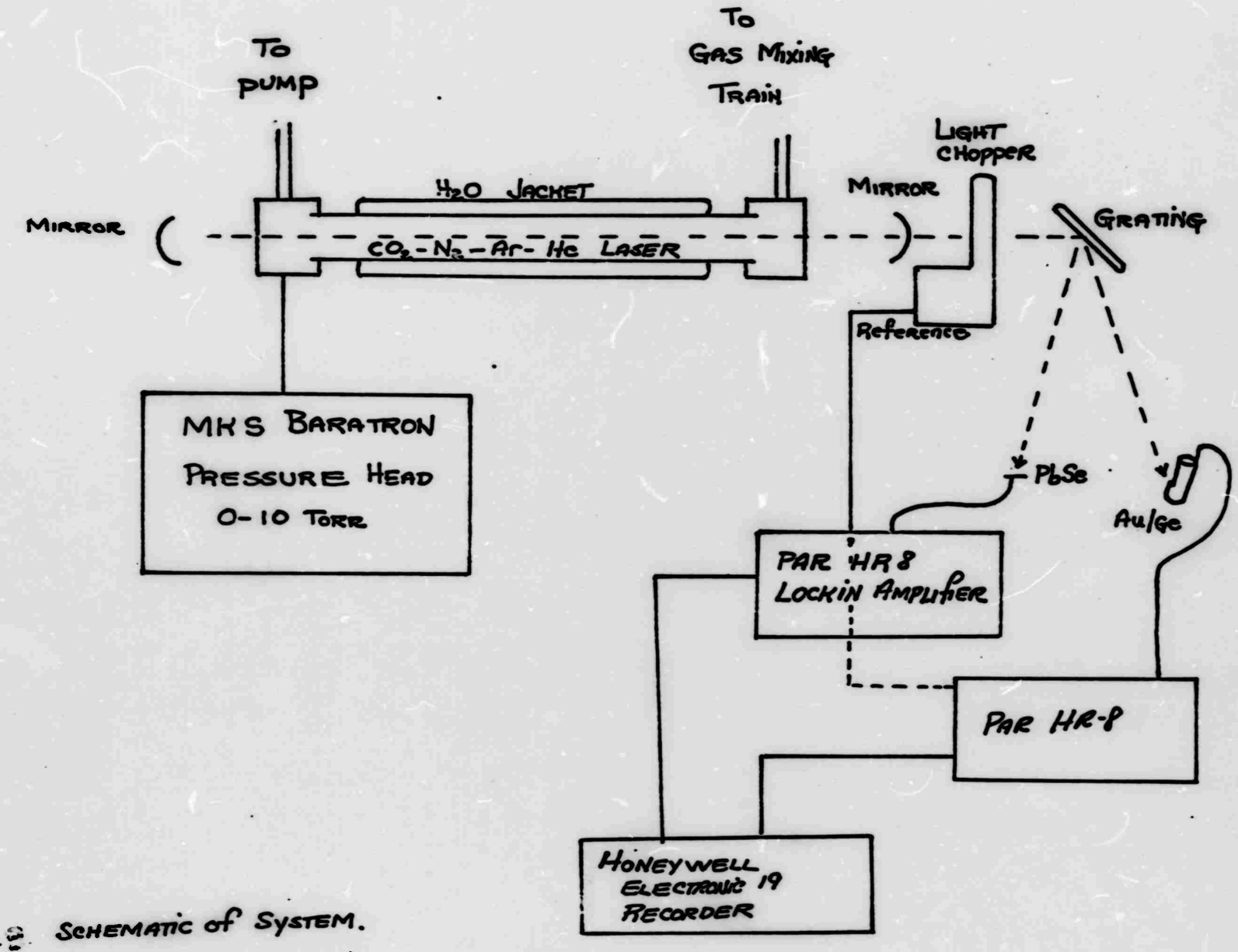


FIGURE 2. SCHEMATIC of SYSTEM.

Effect of Replacing N_2 by CO

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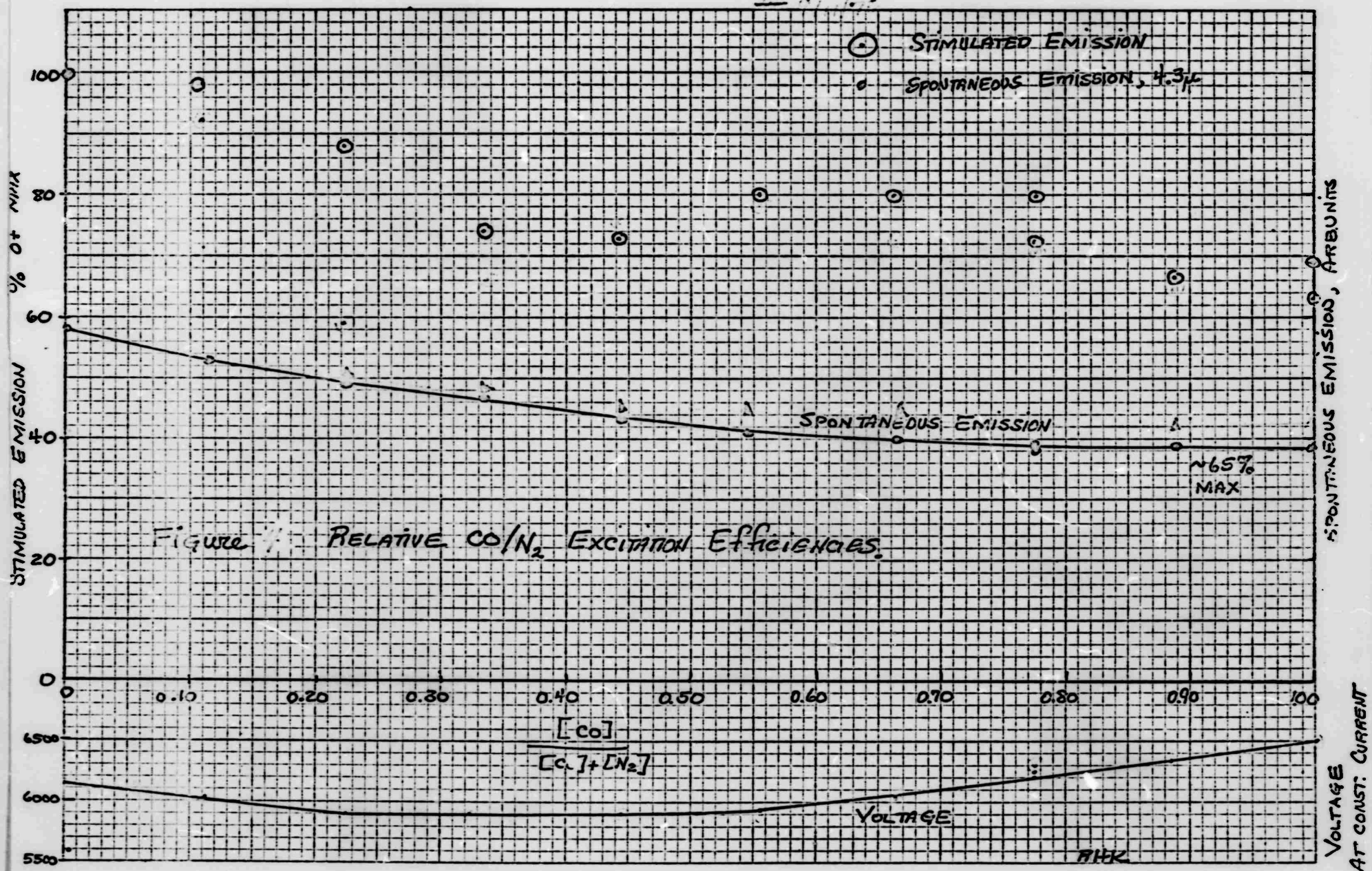

Figure 7. Relative CO/N_2 Excitation Efficiencies.

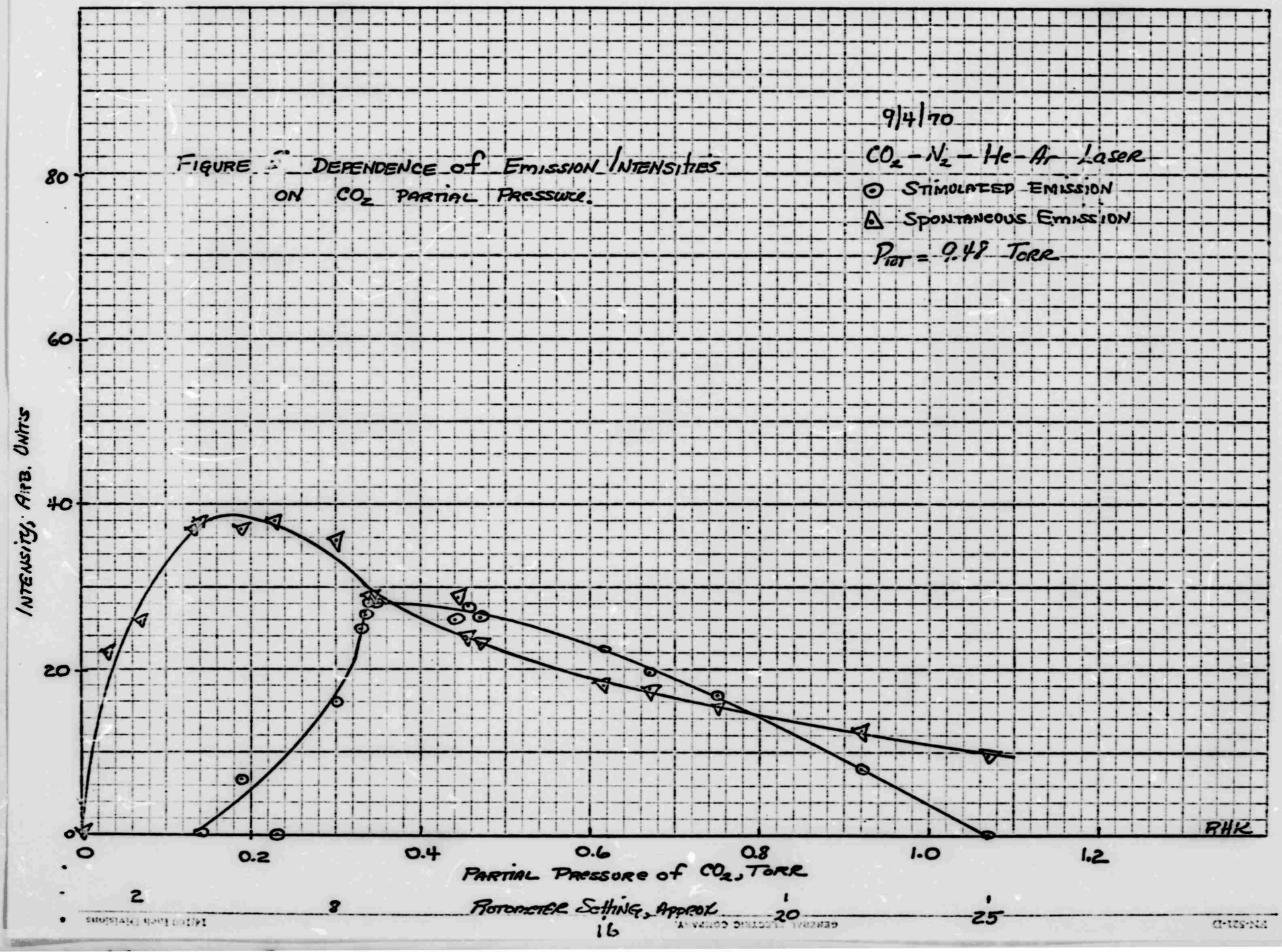
FIGURE 5 DEPENDENCE of EMISSION INTENSITIES ON CO_2 PARTIAL PRESSURE.
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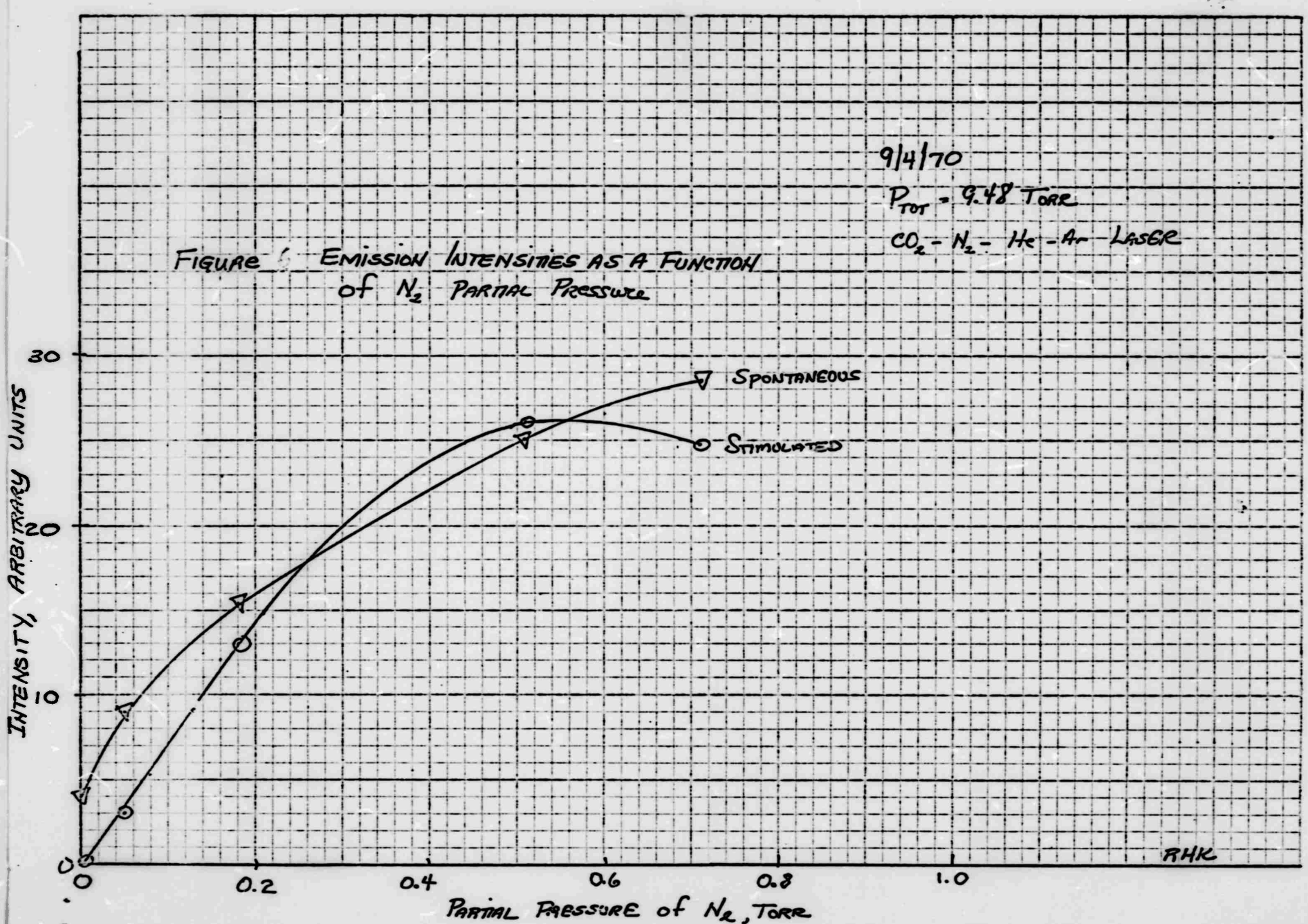
$CO_2 - N_2 - He - Ar$ LASER
⊙ STIMULATED EMISSION
△ SPONTANEOUS EMISSION
$P_{TOT} = 9.48$ TORR
INTENSITY, ARB. UNITS
80
60
40
20
0
0.2
0.4
0.6
0.8
1.0
1.2
PARTIAL PRESSURE of CO_2, TORR
RHK
2
8
ROTOMETER SETTING, APPROX
20
25
16


9/4/70
P_{TOT} - 9.48 TORR
CO_2 - N_2 - He - Ar LASER
FIGURE 1 EMISSION INTENSITIES AS A FUNCTION of N_2 PARTIAL PRESSURE
SPONTANEOUS
STIMULATED
INTENSITY, ARBITRARY UNITS
30
20
10
0
0
0.2
0.4
0.6
0.8
1.0
PARTIAL PRESSURE of N_2, TORR
RHK